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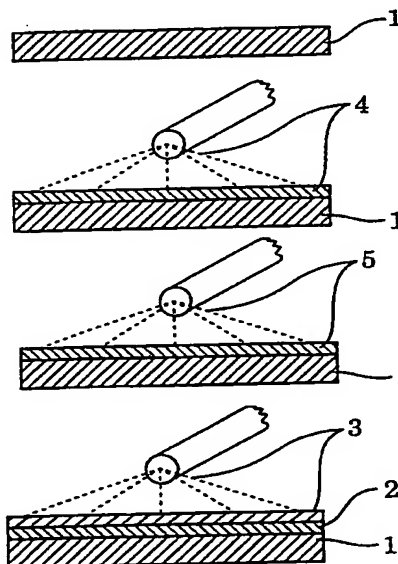
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<p>(21) International Application Number: <b>PCT/US92/10425</b> (22) International Filing Date: <b>3 December 1992 (03.12.92)</b> (30) Priority data: <b>3/320395</b>                      <b>4 December 1991 (04.12.91)</b>    <b>JP</b> (71)(72) Applicant and Inventor (for all designated States except US): <b>SAITO, Tamio [JP/US]; 3114 Alameda de las Pulgas, Menlo Park, CA 94025 (US).</b> (72) Inventors; and (75) Inventors/Applicants (for US only) : <b>NAKASHIMA, Tetsuto [JP/JP]; 2-250-2, Mukaikogane, Nagareyama, Chiba (JP). MOGI, Masayoshi [JP/JP]; 1644-60, Yamasaki, Noda, Chiba (JP). OKADA, Masaki [JP/JP]; 1122-30, Nakanoda, Noda, Chiba (JP). TSUNEMATU, Hironaka [JP/JP]; 1315, Mebuki, Noda, Chiba (JP).</b></p>		<p>(74) Agent: <b>HICKMAN, Paul, L.; Hickman &amp; Associates, P.O. Box 61059, Palo Alto, CA 94306 (US).</b> (81) Designated States: <b>KR, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</b>  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>

(54) Title: **PLASTIC MIRROR AND MANUFACTURING METHOD THEREOF**

(57) Abstract

A plastic mirror comprises plastic substance (1) onto which surface active agent (4) is coated and a silver thin layer (2) which is formed on the surface of the plastic substrate through electroless silver plating after the said coating of the surface active agent. The product is manufactured by applying surface activator onto the surface of plastic substance and then applying silver plating liquid (5) onto the said surface, thereby the silver plating liquid is spread over the surface without repelling to form the thin plastic layer having high-quality and high reflectivity through electroless silver mirror reaction.



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PLASTIC MIRROR AND MANUFACTURING METHOD THEREOFDescription

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Technical Field

This invention relates to a plastic mirror and a manufacturing method therefor,  
10 and is particularly concerned with a mirror made of plastic such as acrylic resin  
(polymethylmethacrylate, methacrylic resin, or PMMA), on which silver is  
electrolessly plated, and to a manufacturing method thereof. The plastic may be  
acrylic resin whose surface has been activated by chemical method, such as coating  
of surface-active agent and/or adsorption of metal of palladium, and/or has been  
15 hardened by coating of hardener such as silica sol, silane coupling agent or  
fluorosilicic acid. This invention provides mirrors which is more lightweight than  
existing glass mirror and is not easily damaged physically, and therefore is very  
safe to be earthquake proof and also less expensive comparing to existing glass  
mirror. This invention also provides mirrors that have higher reflectivity compared  
20 with plastic mirror of aluminum vapor deposition. Through these advantages, this  
invention contributes to the human life in the area of construction, cosmetics,  
electronics and automobile industry.

25 Background Art

Generally, glass mirror is commonly known to have the highest light  
reflectivity. Glass mirror is manufactured by electroless silver plating where silver  
thin film is formed or deposited on one side of transparent glass substrate through  
30 electroless silver-mirror reaction that reduces silver plating solution containing  
ammoniacal silver nitrate with glucose.

The glass mirror made through such a process has always a risk to be broken and to hurt the human body, therefore intensive caution is required to take care of it. Further, a glass mirror can hardly be thin, for example less than 80 mil thickness because of difficulty of manufacturing and handling, therefore it requires to have  
5 certain thickness such as 120 mil. Especially in the case of large glass mirror, weight of mirror is significantly increased so that transportation and handling thereof become cumbersome; the best attention must be given to transportation and handling of glass mirror.

For solving the above problems, such as fear of hurt or difficulty of handling,  
1 0 it has been expected that mirror is manufactured with plastic substance. As a manufacturing method, in the first place it is thought electroless silver plating or silver mirror reaction which is normally used in manufacturing of glass mirror.

However, if electroless silver plating method is applied to plastic substance, silver can not be easily deposited on the surface of the plastic substance. Even if  
1 5 somehow silver metal layer could be deposited, it is rough, tarnished and reflects little light. Further, the deposited silver metal layer does not adhere to the plastic surface strongly, and is easily peeled off by rinsing. In addition to that, if it is flowed onto the plastic surface, the solution is repelled and never be spread over the surface uniformly, therefore large area uniform silver layer cannot be formed.  
2 0 Because of those technological difficulty it is commonly believed that a mirror using plastic substance can not be manufactured by electroless silver plating.

There was a report regarding a trial to give plastic substrate a coat of dispersion colloid of silver particle. It was, however, unsuccessful to manufacture plastic mirror with high light reflectivity.

2 5 Therefore, aluminum vapor deposition, where aluminum metal is evaporated under vacuum on a transparent plastic substance is only used at present to manufacture plastic mirror.

The plastic mirror manufactured by aluminum vapor deposition is inferior to glass mirror manufactured by electroless silver plating in light reflectivity, and

therefore the plastic mirror looks dark. Further, the plastic mirror manufactured by aluminum vapor deposition tends to have many pin holes, so people feels that it is mirror of poor quality. Therefore the plastic mirror manufactured by aluminum vapor deposition is used as reflector rather than as mirror in a room. As vapor  
5 deposition requires vacuum system, plastic mirror made by aluminum vapor deposition is more expensive in respect with manufacturing cost than glass mirror made by electroless silver plating.

#### 1 0 Disclosure of the Invention

An object of the present invention is to solve the above-mentioned problems and provide a plastic mirror which can be easily manufactured at low cost and is light, safe and highly reflective, and a method for manufacturing it.

1 5 According to the present invention, there may be provided an improved plastic mirror comprising plastic substance, surface-active agent coated onto the surface of said plastic substance and a silver thin layer which is deposited on said surface-active agent coated surface by electroless silver plating.

According to the present invention, there may be provided a method for  
2 0 manufacturing a plastic mirror which comprising a step of depositing silver layer onto the surface of plastic substance after surface-active agent is applied onto the said plastic substance.

According to the present invention, the surface of plastic substance may be activated prior to coating the surface-active agent.

2 5 In addition, according to the present invention, the color of the plastic substance can be transparence, colored transparence, opalescence, glassy sky-blue transparence. A plastic substance having treated surface may be used. In this case, the surface treatment of plastic substance is performed by etching, blowing plasma

jet, silica coating and/or low reflection coating. Preferably, hardener is coated on the plastic substance to provide the treated surface.

The plastic substance can be formed to a plate, substrate or film or any topological derivative such as parabolic, curved, bent, dimpled, bumped, waved, saw-edged, notched or swelling shape.

By coating surface-activate agent onto the surface of plastic substance, hydrophobic surface becomes to be hydrophilic surface and silver plating solution will be spread over the surface of plastic substance without repelled. Therefore, uniform silver layer can be deposited onto the surface of plastic.

10 In the case that the surface of the plastic substance has been activated by adsorption of metal such as palladium prior to coating the surface-activate agent onto the surface of plastic substrate, electroless silver plating can be carried out more easily.

The inventors had tried to make a plastic mirror having high reflectivity by electroless silver plating, however it had been unsuccessful. Because the surface of the plastic mirror can not be uniformly wetted over with plating solution, it was extremely difficult to uniformly plate the surface of plastic substance. Thus, the inventors had failed to manufacture a plastic mirror that is highly reflective.

Even if silver thin layer was deposited on surface of plastic substance by electroless silver-mirror reaction that reduces silver plating solution containing ammoniacal silver nitrate with glucose, the silver has not been deposited easily. Even if it is deposited, only rough, tarnished and low reflective silver layer could be obtained. Further the silver layer cannot adhere to the surface of the plastic and easily peeled off such a low stress as rinsing. Furthermore the silver plating solution was repelled by the plastic surface, and therefore uniform silver plating layer at large area could not be manufactured.

Therefore, the inventors have experimented with various methods, and have invented such a simple method that is capable of manufacturing a highly reflective

plastic mirror. According to this method, a silver thin layer is deposited by electroless silver plating method after surface-active agent is coated.

Plastic mirror manufactured by this method has high reflectivity and high quality which is the same level of glass mirror. The inventors think the cause making it possible to realize the high quality mirror as follows.

Coating aqueous solution containing surface-active agent changes hydrophobic surface of plastic to hydrophilic surface. Surface-active agent contains hydrophilic group and hydrophobic group in a single molecule. Therefore, surface-active agent sticks to the plastic surface which is hydrophobic at the hydrophobic group of said surface-active agent. This results that the hydrophilic group of surface-active agent is positioned out side of surface of said plastic substance. Under this condition, because the hydrophilic group of surface-active agent spreads the aqueous solution on the surface of plastic substance, the aqueous solution will spread all over the surface of plastic without repelling.

However, because the surface-active agent disturbs the silver-mirror reaction on the surface of plastic substance, the concentration of the surface-active agent in the aqueous solution which is to be coated on the surface of plastic substance shall be as low as possible. Therefore if the aqueous solution contains certain amount of surface-active agent which makes it possible that silver plating solution will be spread uniformly and at the same time not disturbing silver mirror reaction, then uniform silver layer can be deposited.

In the process according to the invention, that is, depositing a silver plating layer on the surface of plastic substance by electroless mirror silver reaction reducing ammoniacal silver nitrate with glucose, if plastic substance is to have hardener coating, the plastic substance becomes easy to be processed by ammoniacal silver nitrate solution and the silver adheres strongly on the surface of the hardener-coated surface of the plastic substance when complex ion of silver in ammoniacal silver nitrate is reduced with glucose. Thus it is possible to form a plastic mirror having the same quality as a high-grade glass mirror.

The hardener contains silane coupling and silica sol. Silica( $\text{SiO}_2$ ) is the main component of glass and therefore, the hardener-coated surface of plastic becomes similar to the surface of glass. Therefore when silver complex in ammonium silver nitrate is reduced with glucose, deposition of silver easily takes place on the surface of plastic and can adhere strongly to the surface of the plastic substance.

In addition to coating hardener, there are some treatment for that electroless silver plating becomes to be caused on the surface of plastic easily. For example, it is activation treatment by coating of silica or adsorption of palladium metal, etching treatment by chromic acid mixture, plasma treatment, low reflection coating.

The color of plastic resin should not be necessarily transparent, but also colored transparent, smoke, opalescent or glass sky blue transparent. Colored part is all over the plastic resin, so that the surface is not affected by the coloring. Therefore, a silver layer deposited on the surface of the colored plastic is in good condition just like that on the transparent plastic.

The plastic mirror manufactured on transparent resin by electroless silver plating has an impression to be slightly yellow comparing to glass mirror, because glass has slightly color of green. Therefore, if the plastic having the similar color of glass is used, it is possible to manufacture a plastic mirror that looks like glass mirror in tone of color can be manufactured.

Furthermore, in case of a plastic mirror smoked with slightly various color, image in mirror does not look like reality, thus it can create calm. Plastic can be easily dyed comparing to glass. The invention makes it possible to manufacture new type of color mirror much easier.

Plastic can be formed in various shape much easier than glass. Mirror, shaped not plane, such as cylindrical, parabolic shaped, can hardly made by vapor deposition. Wet silver plating solution can be applied to any shape; it does not depend on the shape of plastic to be processed. In case of using the wet silver plating solution the inside of parabolic shaped plastic substance can be easily plated by silver, which is impossible by vapor deposition methodology.



### Brief Description of the Drawings

Other and further objects, features and advantages of the invention will appear  
5 more fully from the following description of embodiments with reference to  
accompanying drawings. It is to be expressly understood, however, the drawings  
are for purpose of illustration only and is not intended as a definition of the limits of  
the invention.

FIG. 1 is a schematical view of a plastic mirror according to preferred  
1 0 embodiments of the invention,

FIG. 2 is an explanatory view of a manufacturing method according to  
preferred embodiments of the invention,

FIG. 3 is a schematical view of a mid-air plastic mirror according to preferred  
embodiments of the invention.

1 5

### Best Modes for Carrying out the Invention

Hereinafter a plastic mirror and its manufacturing method according to the  
2 0 preferred embodiments of the present invention will be described.

Throughout the first, second and third embodiments described below in details,  
as shown in Fig. 1, a plastic mirror according to the preferred embodiments  
comprises plastic substance 1, silver thin layer 2 and protection layer 3 while the  
last is optional, and additionally, as shown Fig. 2, a manufacturing method of the  
2 5 plastic mirror according to the preferred embodiments comprises the steps of  
applying surface-active agent 4 onto the surface of the plastic substance 1 to activate  
the surface, applying silver plating solution 5 onto the surface-active agent coated  
surface of the plastic substance 1 to deposit the silver thin layer, and depositing the

protection layer 3 onto the silver thin layer for the purpose of protection and sealing of it, while the last step is optional.

In the first embodiment, transparent polycarbonate (PC) is used as plastic resin. This transparent PC is formed into a transparent substrate having the thickness of  
5 10 mil. (0.25 millimeters), 20 mil (0.5 millimeters), 40 mil (1.0 millimeters), or 80 mil (2.0 millimeters).

In order to activate the surface, Tin (II) chloride aqueous solution ( 37% HCl; 1 ml is added to  $\text{SnCl}_2$ , 1.0 g/l ) and palladium chloride aqueous solution ( 37% HCl; 0.1 ml is added to  $\text{PdCl}_2$ , 0.1 g/l ) are to be used.

10 As surface-active agent, straight-chain-alkylbenzene sulfonate, sodium alkylsulfate are used. In this embodiment, solution of surfaceactive agent is prepared by diluting 0.7 ml of dish washing liquid (Mama Lemon of Lion Corp.) which contains 27% surface-active agent, with 1l water (hereinafter referred to as "SAWS" ).

15 As silver plating solution, ammoniacal silver nitrate solution  $\text{AgNO}_3$ , 17 to 51 g/l added excess ammonia (A-Solution), sodium hydroxide aqueous solution  $\text{NaOH}$  40g/l (B-Solution) and glucose aqueous solution  $\text{C}_6\text{H}_{12}\text{O}_6$ , 30g/l (C-Solution) are used.

Said ammoniacal silver nitrate water solution  $\text{AgNO}_3$  added excess ammonia  
20 can be prepared by adding aqueous ammonia slowly to silver nitrate solution until precipitation disappears. further adding concentrated aqueous ammonia (28%) by 14 ml with solution 1l. In the case of silver nitrate being 17g/l, concentrated aqueous ammonia (28%) 28ml is added into water 1l.

In a manufacturing method according to this preferred embodiment the above-  
25 mentioned materials are used. Transparent substrate of polycarbonate (PC) resin is dipped into tin chloride (II) aqueous solution for one minute, then it is dipped in palladium chloride aqueous solution for one minute. This procedure is repeated one more. As palladium metal which has the function of catalyst is deposited on the surface of the plastic in the above procedure, the surface of plastic is activated.

Then, said SAWS is slightly coated onto the surface of the transparent substrate. This application of SAWS is accomplished by, for example, dropping or spraying the SAWS onto the substrate placed horizontally. Because the SAWS is adsorbed onto hydrophobic surface of the substrate so that hydrophilic molecule of the SAWS is positioned to be outside of the surface, and therefore the surface of the said substrate becomes hydrophilic. Accordingly, silver solution can be spread all over the substrate without being repelled from the surface of the substrate.

As the SAWS disturbs the silver plating reaction, the application thereof has to be minimized in volume.

Then, the said A-solution, B-Solution and C-solution are mixed together with the ratio of 4:1:1 at the temperature above 15 Centigrade degrees. The mixed solution as processed (Silver Plating Solution: hereinafter referred to as SPS) is applied (dropped or sprayed) onto the surface which has been just coated by SAWS, and the SPS applied surface is left as it is. The SPS, with the help of SAWS, can be spread over the surface without being repelled and deposit uniformly a silver thin film layer on the surface of said substrate through mirror silver reaction. In order to protect the silver thin film, a copper protection thin layer is formed by copper (II) sulfate aqueous solution and reducing agent (Zinc powder suspension) and then resin is coated onto the copper thin layer for protection and sealing.

If the unplated side of the plastic substrate is looked at, it is proved that the plastic mirror is clear and has high light reflectivity.

Concentration of silver nitrate solution in ammoniacal silver nitrate solution  $\text{AgNO}_3$  added excess ammonia proportionally influences the thickness of silver film layer and thus the reflectivity. In the case of high concentration of silver nitrate solution, silver film layer becomes thick and has high light reflectivity. However, silver nitrate is an expensive material, and therefore, instead of using high concentration of silver nitrate, repeat of silver plating under low concentration of silver nitrate is preferable for economical reason.

Therefore, a highly reflective mirror can be manufactured very easily at a significantly low cost.

5 A plastic mirror is lighter, stronger to mechanical stress and much safer than a glass mirror. Additionally, because a plastic mirror is lighter and safer, it is suitable to be attached to the inside of lid of a compact which comprises capsule containing cosmetic powder. It can be used as a mirror covering a wide area on the wall, and such usage is very difficult in case of glass mirror because of its weight and difficulty of handling. Moreover, a film-shaped plastic mirror can be attached on the wall in the manner similar to that of laminating wall paper.

10 Further, a plastic mirror according to this embodiment can be formed in any shape and stuck to any curved or waved surface of construction after manufactured. For example, as shown in Fig. 3 it is possible to form mirror plastic mirror.

And, in the said manufacturing process, activation of plastic surface by palladium could be eliminated. In this case, a manufactured mirror has lower  
15 reflectivity, however it still can be used in limited practical application. In the case of using polycarbonate (PC) resin, a relatively highly reflective mirror can be manufactured, even though the activating process is eliminated.

In the present embodiment a dish washing liquid called Mama Lemon sold by Lion Corp. containing surface-active agent straightchain-alkylbenzen sulfonate and  
20 sodium alkylsulfate as anionic surfactant, in 27% is used. However, other dish washing liquid or other surface-active agent can be used. It can be used in this embodiment as surface-active agent of anionic surfactant, soap (alkali salt of fatty acid) or alkyl naphthalenesulfonate, and cationic surfactant such as primary amine and quaternary ammonium compound, and nonionic surfactant such as  
25 polyethylene glycol derivative, sugar ester, and amphoteric surfactant such as higher fatty amino acid.

In the present embodiment a polycarbonate (PC) resin is used as a plastic resin. However, poly-vinyl-chloride (PVC) resin, methacrylic resin (PMMA), polystyrene(PS) resin or styrene acrylonitrile copolymer (SAN) resin may be used.

In this embodiment, substrates having a thickness of 10 mil, 20 mil, 40mil, and 80 mil are used. However, a substrate having a different thickness can also be used.

Further, in this embodiment, a plate of plastic resin is used as plastic resin  
5 substrate. However, film of plastic resin can also be used. In this case, similar to the planar substrate, a plastic mirror can be manufactured easily. In case of using the film of plastic substrate, the film thickness can be in the range of 1 mil (0.2 millimeters) to 20 mil (0.5 millimeters), although more thin or more thick film can be used. As examples of film of plastic, polyolefin series such as polyethylene  
10 (PE), polypropylene (PP), polyester series film such as polyethylene terephthalate(PET), polybutylene terephthalate (PBT), polyamide series film such as 6-nylon, 6,6-nylon, 12-nylon, cellulosic plastics such as nitrocellulose and cellulose acetate (CA) and poly(vinyl alcohol) (PVC) can be used. In order to use silver plated film as a mirror, the back side of the film is stuck on flat plate to  
15 maintain flat. It also can be directly laminated onto the wall surface of a structure or building without attaching the strengthening substrate.

Now, the second preferred embodiment will be described.

In this embodiment transparent polycarbonate (PC) is used as a plastic resin. The said resin is formed into transparent plate having thickness of 10 mil (0.25  
20 millimeters), 20 mil (0.5 millimeters), 40 mil (1.0 millimeters), 80 mil (2.0 millimeters), 120 mil (3.0 millimeters), 160 mil (4.0 millimeters).

Surface-active agent used in this embodiment is the same as that in the first embodiment.

As a silver plating solution, ammoniacal silver nitrate solution  $\text{AgNO}_3$  10 to 17  
25 g/l added excess ammonium (D-Solution), sodium hydroxide aqueous solution  $\text{NaOH}$  40g/l (E-Solution) and glucose aqueous solution  $\text{C}_6\text{H}_{12}\text{O}_6$  30g/l (F-Solution) are used.

In order to activate the surface, the mixed catalyst solution is used in the present embodiment. Dilute hydrochloric acid (37%  $\text{HCl}$  is diluted with water until the total

volume of solution is 1l) and mixed catalyst solution ( 60 to 320 ml of 37% HCl, 1g of  $\text{PdCl}_2$  and 22 to 50g of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  are diluted with water until the total volume of solution is 1l) and accelerator solution ( 40g of sodium hydroxide is diluted with water until the total volume of solution is 1l) are used.

- 5 Ammoniacal silver nitrate solution  $\text{AgNO}_3$  added excess ammonia used in this embodiment is the same as that used in the first embodiment. Namely, in order to prepare ammoniacal silver nitrate solution  $\text{AgNO}_3$  added excess ammonia, aqueous ammonia is added slowly to silver nitrate solution until precipitation disappears and further concentrated aqueous ammonia (28%) 14ml with solution 1l is added. In  
10 the case silver nitrate is 17g/l, total of concentrated aqueous ammonia (28%) 28ml is added into water 1l.

In this embodiment the above-mentioned materials are used in the process similar to that of the first embodiment to form a plastic mirror.

- After dipped into the diluted hydrochloric acid for about ten seconds, a plate of  
15 polycarbonate resin is dipped into the mixed catalyst solution for two to three minutes. Then, it is dipped into the accelerating solution for five minutes and washed and rinsed with water. In the above processes, palladium having catalytic activity is absorbed on the surface of plastic resin.

- Then, the SAWS is coated slightly onto the surface of polycarbonate plate.  
20 This application of SAWS may be accomplished by dropping or spraying the SAWS onto the substrate placed horizontally. In this procedure, the SAWS is adsorbed onto hydrophobic surface of the substrate so that hydrophilic molecule of the SAWS is positioned to be outside of surface, and therefore the surface of the said substrate becomes hydrophilic. Accordingly, silver solution can be spread all  
25 over the substrate without being repelled from the surface of the substrate. The SAW has to be minimized in volume.

Thereafter, the said D-solution, E-Solution and F-solution are mixed together with the ratio of 4:1:1 at the temperature above 15 degrees Centigrade. The mixed solution as processed (Silver Plating Solution: hereinafter referred to as SPSII) is

applied (dropped or sprayed) onto the surface of the plate which has been just coated by the SAWS. The SPSII can be spread over the surface without being repelled and deposit uniformly a silver thin film layer on the surface of the plate. In order to protect and seal the said silver thin film, a copper thin layer is deposited on the silver thin film and coating resin is coated on the copper thin layer.

The plastic mirror manufactured according to this embodiment has the same effect and advantages as those of the first embodiment.

Although the color of the plastic resin is transparence in this embodiment, colored transparence, smoke, opalescence, glass sky blue transparence of plastic can be also used.

And, in this embodiment also, the activating process of the plastic surface could be eliminated. In this case, manufactured plastic mirror has lower reflectivity, however it still can be used in limited practical application. However, in the case of using polycarbonate (PC) resin being used, a relatively highly reflective mirror can be manufactured, even though the activating process is eliminated.

In this embodiment, the polycarbonate resin is used. However other plastic can be also used. Plastic resin such as polyvinyl chloride (PVC) resin, methacrylic resin (PMMA), polystyrene (PS) resin, styrene acrylonitrile copolymer (SAN) resin can be used.

In this embodiment, plates of plastic resin having thickness of 10 mil, 20 mil, 40mil, 80 mil are used. However, a plate of plastic resin of more thin or more thick can be also used.

Now, the third preferred embodiment will be described.

In the present embodiment, acrylic resin (i.e polymethylmethacrylate, methacrylic resin or PMMA) on which hardener has been coated is used. The acrylic resin is formed into a plate having thickness of 20mil, 40mil, 80mil, 160mil, 200 mil (or other thickness if necessary) and is coated by hardener which contains silane coupling agent and silica sol or fluorosilicic acid.

As surface-active agent, similar to the first embodiment, straightchain-alkylbenzene sulfonate, sodium sulfonate are used. In this embodiment, solution of surface-active agent (SAWSIII) is prepared by diluting dish washing liquid (Mama Lemon of Lion Corp.) containing 27% surface-active agent 0.3 ml to 2.0 ml  
5 with 1l water.

As silver plating solution, ammoniacal silver nitrate solution  $\text{AgNO}_3$  7 to 34 g/l added excess ammonia (G-Solution), sodium hydroxide aqueous solution  $\text{NaOH}$  20g/l (H-Solution) and glucose aqueous solution  $\text{C}_6\text{H}_{12}\text{O}_6$  3 to 15g/l (I-Solution) are used.

10 Ammoniacal silver nitrate solution  $\text{AgNO}_3$  added excess ammonia used in this embodiment is the same as that used in the first embodiment. Namely, it can be prepared by adding aqueous ammonia slowly to silver nitrate solution until precipitation disappears, further adding concentrated aqueous ammonia (28%) 14 ml/l with solution 1l. In the case of silver nitrate being 34g/l, concentrated aqueous  
15 ammonia (28%) 56ml is added into water 1l.

A plastic mirror according to this embodiment can be manufactured by using the above-mentioned materials and solutions.

The SAWSIII is slightly coated onto the surface of the hardener coated acrylic resin (PMMA). This application of the SAWSIII may be accomplished by  
20 dropping or spraying the SAWSIII onto the plate resin placed horizontally. In this procedure, the surface of hardener coated acrylic resin becomes hydrophilic and silver plating solution can be smoothly spread all over the surface of the resin without being repelled from the surface of said substrate. The SAWSIII has to be minimized in volume.

25 Then, the G-solution, H-Solution and I-solution are mixed together with the ratio of 1:1:1 at the temperature above 15 degrees Centigrade. The mixed solution as processed or Silver Plating Solution (SPSIII) is applied (dropped or sprayed) onto the surface of hardener coated acrylic resin which has been just coated by SAWSIII. The SPSIII, with the help of SAWSIII, can be uniformly spread over



the surface without being repelled and deposit uniformly a silver thin film layer on the surface of the plate. In case of an acrylic substrate having large hardener coated surface, the G-solution, H-Solution and I-solution can be sprayed with the same volume separately on the same area of the surface of said hardener coated acrylic resin to mix said solution together on it. As a sequence of spraying on the surface, one option is to spray the G-solution and H-solution then spray the I-solution. Other option is to spray all of solution at the same time.

In order to protect the silver thin film, a copper thin layer is deposited thereon, and coating resin is coated on the copper thin layer for the purpose of protection and sealing. In order to increase the thickness of the silver plating film the silver plating solution is applied repeatedly such as two to three times.

A plastic mirror manufactured in accordance with this embodiment has the same effect and advantages as those in the first and second embodiments. In addition, since the surface of the plastic resin is coated by hardener agent, the mirror according to this embodiment is hardly be damaged.

A plastic mirror comprising the hardener coated acrylic resin has advantage in optical characteristics, therefore it can be applied to backlight optical guide for liquid crystal display.

In this embodiment the hardener agent can be coated on either one side or both sides of the acrylic resin.

The color of plastic resin is not limited only to transparency, but also colored transparency, smoke, opalescence, glassy sky blue transparency. Furthermore, in the case that the plastic having the similar color to glass is used to manufacture, a plastic mirror looks like glass mirror in tone of color.

As the plastic resin can be easily dyed variously, many types of plastic mirrors can be manufactured. In the case of smoke plastic, a plastic mirror manufactured looks calm. In the case of using the plastic resin of other colored transparency a fantasy plastic mirror can be manufactured. The invention makes it possible to manufacture the various color mirrors easily

In this embodiment an acrylic resin is used. However, other plastic resin such as polyvinyl chloride (PVC) resin, polycarbonate resin (PC) resin, polystyrene (PS) resin or styrene acrylonitrile copolymer (SAN) resin can be used.

5 In this embodiment, hardener coated acrylic resin is used. However, other treated plastic resin can be used. Inorganic material such as glass thin film can be formed onto the surface of plastic resin. Etched plastic with chromium acid solution, plasma treated plastic for making the surface of plastic to be hydrophilic or plastic coated with low reflective material for reducing the reflection from the surface of plastic can also be used.

10 In case of using silica coated plastic resin, the coating is processed at the low temperature, and therefore the heat treatment is not required. Therefore, even if the plastic substrate is molded plastic formed to a sophisticated shape, it can also be coated without transformation. The application of silica coating hardens the surface of plastic substrate just like the coating of hardener, and therefore it can provide a plastic mirror having advantages in lowering abrasion and scratch. Silica coating makes silver plating easier even though the plastic surface is not treated by palladium salt. The hardener coated plastic has the same advantages.

15 In case of using plastic which is coated by low reflective material, the reflection on the surface is reduced and the transparency is increased. Therefore, the light can be completely reflected on the surface of silver layer in mirror and it avoids doubled image and increases the transparency of mirror which provides comfortable feeling. Herein, low reflective material coating means that three layers of significantly higher refractive index and significantly lower refractive index comparing to substance are alternately coated on the said plastic surface to prohibit reflection almost completely.

20 Plastic resin can be formed into various shapes much easier than glass. A plastic mirror can be bent into non-planar shapes such as cylindrical shape after manufactured. Moreover, a plastic mirror having any shape such as parabola shape can be manufactured using silver plating solution, because the inside and/or outside

of the plastic having the parabolic shape can easily be plated by silver plating but it can hardly be formed by vapor deposition or sputtering methodology.

In case of rear-under view mirror such as disclosed in Japan Patent Application Kokai No. 60-139549 equipped with an automobile for seeing the side and lower  
5 front thereof, two separate mirrors were combined to give both rear side view and low side view. However, according to this invention it can be provided a mirror to give both of them with a single body. Furthermore, single body mirror where a convex part with a large radius for rear side view and the other convex part with a small radius for lower side view can be made very easily, even though the shape is  
10 too complicated to be made by glass. Also optical guide for microscope and hemisphere or parabolic shaped mirror can be made easily. Furthermore, the inside of caved plastic article (e.g. caved sphere or caved doll) can be plated very easily to manufacture a caved mirror.

As described above, according to the present invention a highly reflective plastic  
15 mirror can be provided very easily at a low cost.

From the invention thus described, it will be obvious that the invention may be varied in many ways. Such variations are not to be regarded as a departure from the spirit and scope of the invention, and all such modifications as would be obvious to one skilled in the art are intended to be included within the scope of the following  
20 claims.

Claims

1. Plastic mirror comprising:  
plastic substance (1) onto which surface-active agent (4) is coated; and  
5 silver thin film layer (2) which is deposited onto said surface-active agent coated  
plastic substance by electroless silver plating.
2. Plastic mirror according to Claim 1, in which the surface-active agent is anionic  
surfactant such as straight-chain alkylbenzene sulfonate, sodium alkylsulfate, alkali  
10 salt of fatty acid, alkylnaphthalenesulfonate, cationic surface such as primary  
amine, quaternary ammonium compound, nonionic surfactant such as polyethylene  
glycol derivative, sugar ester, or amphoteric surfactant such as higher fatty amino  
acid.
- 15 3. Plastic mirror according to any of Claims 1 and 2, in which said plastic  
substance is polycarbonate (PC), acrylic resin such as polymethyl methacrylate,  
methacrylic resin or PMMA; polyvinyl chloride (PVC); polystyrene (PS); styrene  
acrylonitrile copolymer (SAN); polyolefin series such as polyethylene (PE),  
polypropylene (PP); polyester series such as polyethylene terephthalate (PET),  
20 polybutylene terephthalate (PBT); polyamide series such as 6-nylon, 6.6-nylon, 12-  
nylon; cellulosic plastics such as nitrocellulose and cellulose acetate (CA); or  
polyvinyl alcohol (PVC).
- 25 4. Plastic mirror according to any of Claims 1 to 3, in which the surface of said  
plastic substance is activated by adsorption of metal such as palladium prior to the  
said surface-active agent is coated onto said surface of the plastic substance.

5. Plastic mirror according to any of Claims 1 to 4 in which said plastic substance has the color of clearness, transparence, colored transparence, smoke, opalescence, or glassy sky blue transparence.
- 5 6. Plastic mirror according to any of Claims 1 to 5, in which the surface treatment of the plastic substance has been performed by etching, blowing plasma-jet, silica coating and/or low reflection coating.
7. Plastic mirror according to any of Claim 1 to 6, in which hardener is coated on  
1 0 the surface of said plastic substance.
8. Plastic mirror according to any of claims 1 to 7, the shape of said plastic substance is particularly formed into substrate, board, plate, sheet or film.
- 1 5 9. Plastic mirror according to any of Claims 1 to 8, in which said plastic substance is transformed into the shape of mid-air, and said silver thin film is deposited onto inside surface or outside surface of the transformed plastic substance by electroless silver plating.
- 2 0 10. Plastic mirror according to any of Claims 1 to 9, in which said plastic substance is particularly formed to be curved, bent, dimpled, roughed, saw-edged, notched, waved or swelling shape.
11. Plastic mirror according to any of Claims 1 to 10, in which the silver plating  
2 5 solution comprises ammoniacal silver nitrate solution  $\text{AgNO}_3$  17 to 51g/l added excess ammonia (A-solution), sodium hydroxide aqueous solution  $\text{NaOH}$  40g/l (B-solution) and glucose aqueous solution  $\text{C}_6\text{H}_{12}\text{O}_6$  30g/l (C-solution), and is prepared by mixing the A-solution, B-solution and C-solution with the ratio of 4:1:1 in volume.

12. Plastic mirror according to any of Claims 1 to 11, in which the silver plating solution comprises ammoniacal silver nitrate solution  $\text{AgNO}_3$  7 to 34g/l added excess ammonia (D-solution), sodium hydroxide aqueous solution  $\text{NaOH}$  20g/l (E-solution) and glucose aqueous solution  $\text{C}_6\text{H}_{12}\text{O}_6$  15g/l (F-solution), and is prepared by mixing the D-solution, E-solution and F-solution with the ratio of 1:1:1 in volume.

13. Plastic mirror according to Claim 12 in which said D-solution, E-solution and F-solution is sprayed onto the plastic substance, where at least D-solution is sprayed from a separate nozzle.

14. Plastic mirror according to Claim 7, in which the plastic substance is acrylic resin and the hardener comprises silica sol, silane coupling agent or fluorosilicic acid.

15. Manufacturing method of a plastic mirror in which silver layer (2) is deposited onto the surface of plastic substance (1) by electroless silver plating after surface-active agent (4) is coated onto said surface.

20

16. Manufacturing method of a plastic mirror according to Claim 15, in which said surface-active agent is anionic surfactant such as straightchain alkylbenzene sulfonate, sodium alkylsulfate, alkali salt of fatty acid, alkyl-naphthalenesulfonate, cationic surfactant such as primary amine, quaternary ammonium compound, and/or nonionic surfactant such as polyethylene glycol derivative, nonionic surfactant such as polyethylene glycol derivative, sugar ester, or amphoteric surfactant such as higher fatty amino acid.

25

17. Manufacturing method of a plastic mirror in according to any of Claims 15 and 16, in which said plastic substance is polycarbonate (PC), acrylic resin such as polymethyl methacrylate, methacrylic resin or PMMA; polyvinyl chloride (PVC); polystyrene (PS); styrene acrylonitrile copolymer (SAN); polyolefin series such as polyethylene (PE), polypropylene (PP); polyester series such as polyethylene terephthalate (PET), polybutylene terephthalate (PBT); polyamide series such as 6-nylon, 6.6-nylon, 12-nylon; cellulosic plastics such as nitrocellulose and cellulose acetate (CA); or polyvinyl alcohol (PVC).
- 10 18. Manufacturing method of a plastic mirror in according to any of Claims 15 to 17, in which the surface of said plastic substance is activated by adsorption of metal such as palladium prior to the said surface-active agent is coated onto said surface of the plastic substance.
- 15 19. Manufacturing method of a plastic mirror according to any of Claims 15 to 18, in which said plastic substance has the color of clearness, transparence, colored transparence, smoke, opalescence, or glassy sky blue transparence.
- 20 20. Manufacturing method of a plastic mirror according to any of Claims 15 to 19, in which the surface treatment of the plastic substance has been performed by etching, blowing plasma-jet, silica coating and/or low reflection coating.
21. Manufacturing method of a plastic mirror in according to any of Claims 15 to 20, in which hardener is coated on the surface of said plastic substance.
- 25 22. Manufacturing method of a plastic mirror according to any of Claims 15 to 21, in which the shape of said plastic substance is particularly formed into substrate, board, plate, sheet or film.

23. Manufacturing method of a plastic mirror according to any of Claims 15 to 22, in which said plastic substance is transformed into the shape of mid-air (20), and said silver thin film (22) is deposited onto inside surface or outside surface of the transformed plastic substance by electroless silver plating.

5

24. Manufacturing method of a plastic mirror according to any of Claims 15 to 23, in which said plastic substance is particularly formed to be curved, bent, dimpled, roughed, saw-edged, notched, waved or swelling shape.

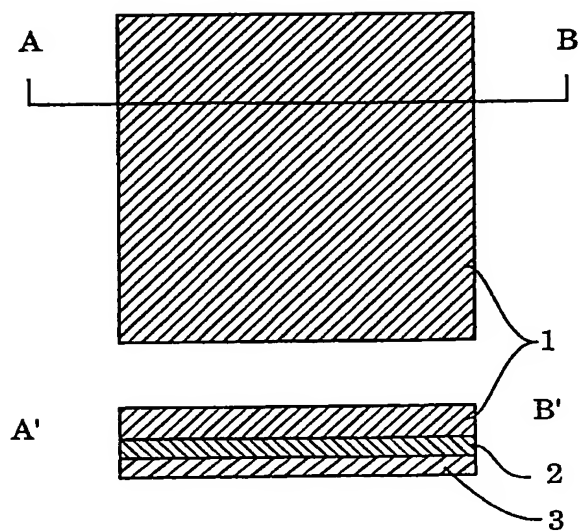
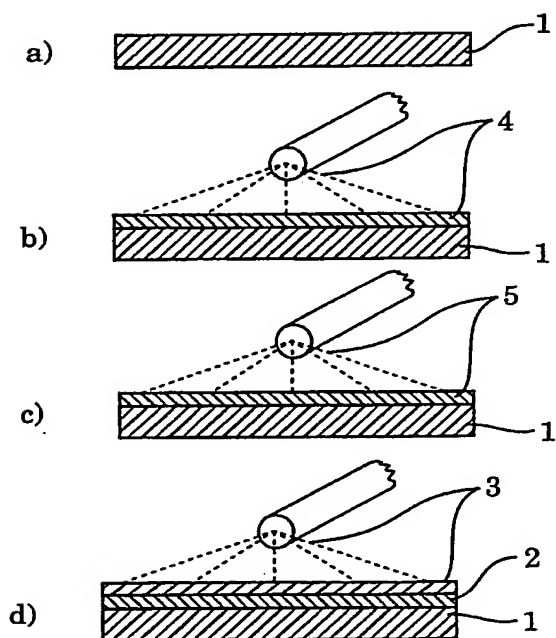
10 25. Manufacturing method of a plastic mirror according to any of Claims 15 to 24, in which the silver plating solution comprises ammoniacal silver nitrate solution  $\text{AgNO}_3$  17 to 51g/l added excess ammonia (A-solution), sodium hydroxide aqueous solution  $\text{NaOH}$  40g/l (B-solution) and glucose aqueous solution  $\text{C}_6\text{H}_{12}\text{O}_6$  30g/l (C-solution), and is prepared by mixing the A-solution, B-solution and C-  
15 solution with the ratio of 4:1:1 in volume.

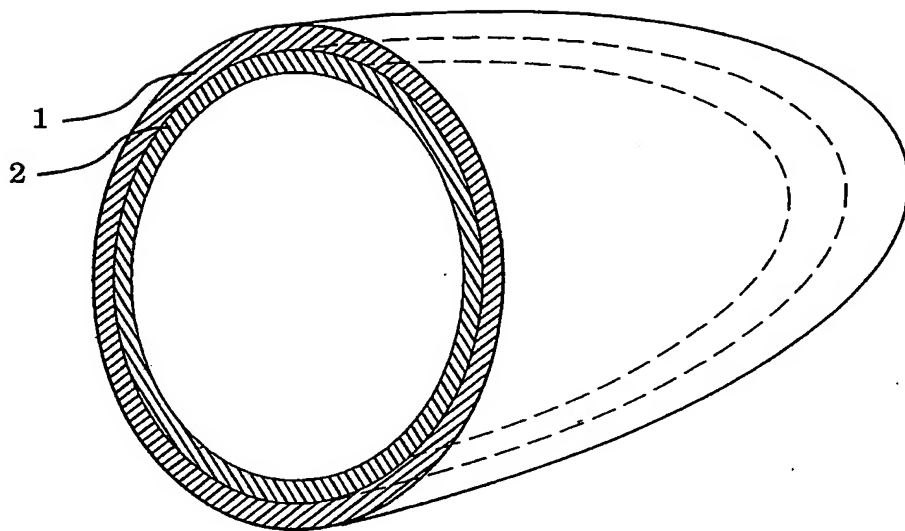
26. Manufacturing method of a plastic mirror according to any of Claims 15 to 25, in which the silver plating solution comprises ammoniacal silver nitrate solution  $\text{AgNO}_3$  7 to 34g/l added excess ammonia (D-solution), sodium hydroxide aqueous  
20 solution  $\text{NaOH}$  20g/l (E-solution) and glucose aqueous solution  $\text{C}_6\text{H}_{12}\text{O}_6$  15g/l (F-solution), and is prepared by mixing the D-solution, E-solution and F-solution with the ratio of 1:1:1 in volume.

27. Manufacturing method of a plastic mirror according to Claim 26, in which said  
25 D-solution, E-solution and F-solution is sprayed onto the plastic substance, where at least D-solution is sprayed from a separate nozzle.



28. Manufacturing method of a plastic mirror according to Claim 21, in which the plastic substance is acrylic resin and the hardener comprises silica sol, silane coupling agent or fluorosilicic acid.

*Fig. 1**Fig. 2*



*Fig. 3*

**SUBSTITUTE SHEET**

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US92/10425

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :B32B 27/36

US CL :428/412, 522, 516, 480, 474.4, 458, 459, 461, 463

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/412, 522, 516, 480, 474.4, 458, 459, 461, 463

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS-(L1) Plastic (2W) mirror

(L2) Polycarbonate or PMMA or PVC or polystyrene or polyamide

(L3) (Thin or silver) film

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,242,413 (TWAHASHI ET AL) 30 DECEMBER 1980. See Claim 5.	1, 2
A	US, A, 4,242,412 (FUNAKI ET AL) 30 DECEMBER 1980. See column 5, lines 30-60.	1, 2

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be part of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

23 FEBRUARY 1993

Date of mailing of the international search report

08 APR 1993

Name and mailing address of the ISA/US  
Commissioner of Patents and Trademarks  
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# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US92/10425

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 3-14 AND 17-28  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.  
☐ No protest accompanied the payment of additional search fees.